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DESCRIPTION

CERAMIC COMPOSITION

Technical Field

The present invention relates to ceramic compositions. In particular, it relates to a ceramic composition usable as, for example, a material for a multilayer substrate used for propagation of signals in a high-frequency band.

Background Art

Recent years saw development in high-speed, large-capacity data communications and cellular communications. With respect to multilayer substrates having integrated circuits, this development led to not only size-reduction and increased density but also investigations as to use of signals having frequencies in a high-frequency band ranging from, for example, several ten megahertz to several hundred gigahertz. While ceramic compositions are used in these multilayer substrates, it is desirable that the ceramic compositions be made of a material (high-frequency band material) compatible with signals in the high-frequency band.

Typically, alumina (Al_2O_3) has been primarily used as the ceramic composition for the high-frequency band. As the density of the integrated circuits increases, there has been developed a process of making a multilayer substrate

including an integrated circuit, the process including stacking a plurality of green sheets composed of unsintered Al_2O_3, each green sheet having a conductor paste that contains a material for metal wiring applied by printing, and then simultaneously baking the green sheets and the conductor paste. Since Al_2O_3 sinters at a temperature as high as 1,500°C to 1,600°C, a high melting point-metal, such as tungsten or molybdenum, which can withstand such a high temperature, has been required as the material for the metal wiring of the integrated circuit.

The multilayer substrate has a problem in that it requires a large amount of energy since the sintering temperature is high, thereby increasing the manufacturing cost. Since the thermal expansion coefficient of Al_2O_3 is larger than that of the IC chip, such as a silicon chip, in the integrated circuit, the multilayer substrate may suffer from cracks depending on the operating temperature of the multilayer substrate. Furthermore, since the relative dielectric constant of Al_2O_3 is large, the rate of signal propagation in the integrated circuit has been low. Since the specific resistance of a high melting point-metal, such as tungsten or molybdenum, is large compared to that of Cu or Ag, which is suitable as a material for the metal wiring, the conductor loss due to the resistance of the metal wiring itself has also been large.

In view of the above, various ceramic compositions each in which a filler is incorporated in a glass composition have been developed as the material for multilayer substrates. Multilayer substrates using such ceramic compositions can be sintered at a temperature lower than that when Al_2O_3 is used. Thus, it becomes possible to simultaneously sinter the ceramic compositions and the material for metal wiring, such as Cu or Ag, having a smaller specific resistance. Furthermore, since the filler is contained in the glass composition, the change in shape of the ceramic composition can be reduced, and the strength of the ceramic composition can be increased.

For example, Japanese Examined Patent Application Publication No. 3-53269 described an example of such a ceramic composition, prepared by sintering a mixture of a CaO-SiO_2-Al_2O_3-B_2O_3 glass composition and 50 to 35 mass% of Al_2O_3 as a filler at 800°C to 1,000°C. Japanese Patent No. 3277169 discloses a ceramic composition containing 0 to 10 mol% of Al_2O_3 as a filler and a glass composition including 50 to 67 mol% of B_2O_3, 2 to 3 mol% of an oxide of an alkali metal element, 20 to 50 mol% of an oxide of an alkaline earth metal element, and 2 to 15 mol% of an oxide of a rare earth element. Japanese Unexamined Patent Application Publication No. 9-315855 discloses a ceramic composition containing an oxide of a rare earth element, Al_2O_3, CaO, and

TiO_2, and in which the compounding ratio of these components is limited within a particular range.

The performances required for the ceramic composition for the high-frequency band include a low dielectric loss tanδ in the high-frequency band and a small absolute value of the temperature coefficient τ_f of the resonant frequency.

In other words, the loss in the course of signal propagation in the high-frequency band is preferably as small as possible. Thus, it is desirable that the dielectric loss tanδ of the ceramic composition in the high-frequency band be small, i.e., that the Q value (1/tanδ) be large. Moreover, in order to yield stable performance from the ceramic composition serving as a dielectric member despite a temperature change, it is desirable that the absolute value of the temperature coefficient τ_f of the resonant frequency be small, i.e., that the temperature dependence of the resonant frequency be low.

Disclosure of Invention

Under the above-described circumstances, an object of the present invention is to provide a ceramic composition that can be sintered at a low temperature and has a small dielectric loss in the high-frequency band and a low temperature dependence of the resonant frequency.

An aspect of the present invention provides a ceramic composition including a glass composition and a filler incorporated in the glass composition, the filler including at least one of Al_2O_3 and TiO_2, wherein the composition of the ceramic composition includes 0.15 to 0.55 mol of **a**, 0.45 to 0.85 mol of **b**, 0.01 to 0.2 mol of an oxide RO of an alkaline earth metal element R, and 0.1 to 0.4 mol of the filler, wherein **a** represents a molar quantity of an oxide Ln_2O_3 of a rare earth element Ln, **b** represents a molar quantity of boron oxide B_2O_3, and **a** + **b** = 1 mol.

Preferably, the ceramic composition includes 0.05 mol or less of tungsten oxide WO_3, wherein **a** represents a molar quantity of an oxide Ln_2O_3 of a rare earth element Ln, **b** represents a molar quantity of boron oxide B_2O_3, and **a** + **b** = 1 mol.

Preferably, the ceramic composition includes 0.0005 to 0.002 mol of an oxide M_2O of an alkali metal element M, wherein **a** represents a molar quantity of an oxide Ln_2O_3 of a rare earth element Ln, **b** represents a molar quantity of boron oxide B_2O_3, and **a** + **b** = 1 mol.

Best Mode for Carrying Out the Invention

The present inventor has conducted various studies on the composition in order to obtain a ceramic composition that can be sintered at a low temperature and has a small

dielectric loss in the high-frequency band and a low temperature dependence of the resonant frequency.

It has been found that a ceramic composition in which a filler composed of an inorganic oxide is incorporated in a glass composition is most suitable as such a ceramic composition. The internal structure of the ceramic composition is a network structure composed of a glass composition filling the gaps between the respective particles of the filler. Since the material usable as the filler is limited within a certain range, the characteristics of the glass composition must be improved to further improve the performance.

Thus, the material for the glass composition was studied first. In particular, the sintering temperature of the glass composition, the compatibility with the filler, the relative dielectric constant, the dielectric loss in the high-frequency band, and the temperature dependence of the resonant frequency were investigated. Of these items, the dielectric characteristic was measured by a dielectric resonator method (short-circuited at both ends of a dielectric resonator), i.e., Hakki & Coleman method, using a cylindrical test sample after sintering.

In general, the dielectric loss is evaluated in terms of Q value, which is obtained by the sharpness of the resonance. The Q value is frequency-dependent and decreases

in proportion to the frequency. In contrast, the resonant frequency changes with the shape and the dielectric constant of the test sample. Thus, the dielectric loss of the ceramic composition is evaluated by comparative assessment in terms of the product fQ of the resonant frequency fo and Q.

As a result of the studies on various glass compositions, it has been found that a glass composition containing a large amount of crystals obtained by mixing an oxide Ln_2O_3 of a rare earth element (also referred to as "Ln") and boron oxide B_2O_3 exhibits a particularly low dielectric loss. In this glass composition, crystals of $LnBO_3$, LnB_3O_6, Ln_3BO_3, or $Ln_4B_2O_9$ appear depending on the compounding ratio, and the phase of these crystals presumably decreases the dielectric loss.

However, in order to adjust the composition of the glass composition composed of only two components, i.e., Ln_2O_3 and B_2O_3, to yield a low dielectric loss, the melting temperature must be increased, and thus, the sintering temperature required for obtaining a dense sinter becomes high. It was found that by adding an adequate amount of an oxide RO of an alkaline earth metal element R (wherein R represents at least one of Mg, Ca, Sr and Ba) to the composition composed of Ln_2O_3 and B_2O_3, the sintering temperature can be decreased without significantly affecting

the dielectric loss.

Here, the target performance of the ceramic composition is set as follows: that the value fQ (fo [GHz] × Q) at around 10 GHz is 15,000 or higher; that the change in resonant frequency with temperature is small; and that the composition can be sintered at a temperature as low as 1,000°C or less, which is the temperature at which metal wiring composed of a highly conductive material, Ag or Cu, can be simultaneously formed to produce a multilayer substrate. The investigations on the composition of the ceramic composition were carried out based these. That the change in resonant frequency with temperature be small is important for the stable operation of the integrated circuit. The resonant frequency was measured while varying the temperature, and the rate of change in resonant frequency (temperature characteristic τ_f) with the varying temperature was evaluated. The target range of the temperature characteristic τ_f of the resonant frequency was set to within ±50 ppm/°C (-50 ppm/°C $\leq \tau_f \leq$ +50 ppm/°C).

It was also found that incorporation of tungsten oxide, WO_3, was effective for decreasing the sintering temperature. It was found that when an excessively large amount of WO_3 was incorporated, the change in resonant frequency with temperature tended to shift toward the negative side.

It was found that incorporation of a small amount of an

oxide M_2O of an alkali metal element M (wherein M represents at least one selected from Li, Na, and K) can further decrease the sintering temperature. In particular, incorporation of M_2O can effectively decrease the sintering temperature when a process of mixing all the starting materials and then sintering the resulting mixture in one step to obtain a ceramic composition is employed.

The filler is important for maintaining the strength of the ceramic composition and the shape during the sintering. Here, one or both of Al_2O_3 and TiO_2 are used as the filler. When the strength is desired, Al_2O_3 is primarily used whereas TiO_2 is primarily used when a large dielectric constant is desired. However, when the amount of filler is excessively large, the sintering temperature must be increased. When the amount of the filler is excessively small, the strength and the shape can no longer be maintained. Thus, the amount of the filler is limited by these factors.

The present invention has been made based on these results of studies by specifically setting the limit of the composition range of the ceramic composition. The ceramic composition of the present invention includes a glass composition and a filler contained in the glass composition and is sintered at a low temperature. The reasons for limiting the amount of each component of the composition are as follows.

Where the content of the oxide Ln_2O_3 of the rare earth element Ln in the ceramic composition of the present invention is represented by **a**, the content of the boron oxide B_2O_3 in the ceramic composition of the present invention is represented by **b**, and **a** + **b** = 1 mol, **a** is 0.15 to 0.55 mol and **b** is 0.45 to 0.85 mol.

These content ranges are necessary for decreasing the dielectric loss in the high-frequency band and for performing low-temperature sintering. When the contents of Ln_2O_3 and B_2O_3 are set as above, excellent dielectric characteristic, i.e., a high fQ value, can be yielded by the generation of crystals represented by $Ln_xB_yO_z$ (wherein x, y, and z each represent an integer). In other words, where **a** + **b** = 1 mol and **a** is less than 0.15 and **b** is more than 0.85, B_2O_3 that cannot form $Ln_xB_yO_z$ enters a liquid phase, thereby increasing the glass phase. Thus, the dielectric loss cannot be decreased. Where **a** + **b** = 1 mol and **a** is more than 0.55 and **b** is less than 0.45, the sintering temperature increases, and a ceramic composition composed of a dense sinter cannot be obtained by the target low-temperature sintering.

Note that any of the rare earth elements represented by Ln can increase the fQ value. Thus, in this invention, one or more rare earth elements can be selected. In particular, when La and/or Nd is used as the rare earth element, an fQ

value higher than that achieved by other rare earth elements can be obtained. However, the sintering temperature and the dielectric constant of the ceramic composition differ depending on the type of rare earth element. Thus, these properties may be adequately adjusted by changing the type of the rare earth element or by changing the content of the oxide RO of the alkaline earth metal element R described below.

The content of the each component described below is indicated in terms of a molar ratio with respect to one mole of the total of Ln_2O_3 and B_2O_3.

The content of the oxide RO of the alkaline earth metal element R is 0.01 to 0.2 mol. At an RO content less than 0.01 mol, the sintering temperature cannot be decreased. At an RO content exceeding 0.2 mol, the temperature characteristic τ_f of the resonant frequency becomes lower than -50 ppm/°C, i.e., excessively shifted toward the negative side, thereby increasing the temperature dependence.

At least one of MgO, CaO, SrO, and BaO may be used as the oxide RO of the alkaline earth metal R. In particular, the fQ value tends to be larger with CaO compared to that with oxides of other alkaline earth metals.

Preferably, tungsten oxide WO_3 is contained in the ceramic composition of the present invention. When WO_3 is contained, a dense sinter can be obtained by low-temperature

sintering, which is the target of the present invention, while increasing the fQ value. In order to achieve such an effect, WO_3 is preferably contained in an amount of 0.05 mol or less and more preferably in an amount of 0.005 to 0.05 mol. At a WO_3 content exceeding 0.05 mol, the fQ value decreases, and the temperature characteristic τ_f of the resonant frequency tends to significantly shift toward the negative side. When the WO_3 content is less than 0.005 mol, the above-described effect is not easily achieved. In the present invention, WO_3 is not an essential component.

The ceramic composition of the present invention preferably contains 0.0005 to 0.002 mol of an oxide M_2O of an alkali metal element M. In this manner, the sintering temperature can be further decreased. In general, a glass composition containing alkali metal ions exhibits a large dielectric loss and a small fQ value due to ionic induction. At an M_2O content of 0.002 mol or less, the fQ value is rarely affected. At an M_2O content of 0.0005 mol or more, the sintering temperature tends to decrease.

One or both of Al_2O_3 and TiO_2 in a total amount of 0.1 to 0.4 mol per mole of the total of Ln_2O_3 and B_2O_3 are contained as the filler. At a filler content less than 0.1 mol, excessive deformation may occur during sintering and the strength of the ceramic composition after the sintering may become insufficient. At a filler content exceeding 0.4

mol, the sintering temperature is increased, and it may be difficult to conduct low-temperature sintering at 1,000°C or less. In order to increase the strength of the ceramic composition, Al_2O_3 may be singularly used or the content of Al_2O_3 may be increased. In order to increase the dielectric constant of the ceramic composition, TiO_2 may be singularly used or the content of TiO_2 may be increased.

There are mainly two methods as the method for producing the ceramic composition of the present invention. According to a first method, powders of starting materials for ceramic composition are prepared, and the powders are respectively weighed to yield a desired composition. The powders are wet-mixed in a ball mill, dried, and calcined at about 800°C. The resulting calcined material is pulverized to obtain a powder. A binder is added to the powder, and the resulting mixture is kneaded and formed into a desired shape to obtain a compact. The compact is heated to remove the binder and sintered to obtain the ceramic composition of the present invention.

According to a second method, powders of starting materials for the glass composition are prepared and respectively weighed to yield a desired composition. The powders are mixed with each other, and the resulting mixture is melted by heating at 1,000°C or higher and rapidly cooled to produce a glass frit. The glass frit is pulverized. The

filler was separately sintered and pulverized to prepare a powder. The glass frit, the filler, and the binder are mixed and kneaded, and formed into a compact. The binder is removed from the compact, and the resulting compact is sintered to prepare a ceramic composition of the present invention. In this second method, with respect to the glass frit containing Al_2O_3 and/or TiO_2 serving as the filler, it is possible to mix and knead the filler and the binder.

The above-described compact can be sintered at a temperature as low as 800°C to 1,000°C. At a sintering temperature less than 800°C, the sintering of the ceramic composition may not be insufficient, and density is not satisfactory. Thus, satisfactory strength may not be exhibited. When the ceramic composition of the present invention is used as a material for a multilayer substrate and is sintered simultaneously with the material for metal wiring, the material for the metal wiring may be heated to a temperature higher than the melting point and may start to melt. However, at a temperature or 1,000°C or less, the sintering can be performed without melting the material for the metal wiring, such as Cu or Ag. It should be noted that when Cu is used as the material for metal wiring, a reducing atmosphere is preferable to avoid possible oxidation, and when Ag is used as the material for metal wiring, the sintering temperature is preferably up to 930°C.

The above-described materials for the ceramic composition are not necessarily oxides as long as they are contained in the ceramic composition by forming oxides after the sintering. Thus, for example, carbonate salts, such as $CaCO_3$, and compounds, such as nitrides, e.g., BN, other than oxides may be used as the starting materials. Although these starting materials may contain impurities, they can be treated as single compounds as long as the impurity content is 5 mass% or less with respect to the mass of the respective compound and the same effects can be still be achieved.

In making a multilayer substrate having an integrated circuit by using the ceramic composition of the present invention, the material after kneading is first formed into sheets to prepare green sheets, and a conductive paste containing the material for metal wiring is applied on each green sheet by printing. A plurality of green sheets with the conductive paste applied thereon is stacked and sintered.

Here, a constraint sintering process in which the compact obtained by stacking a plurality of green sheets having the conductive paste applied thereon by printing is sintered while applying pressure or constraint in the vertical direction may be employed. According to this process, the contraction due to sintering is limited in the vertical direction, i.e., the Z direction, and no

contraction occurs in the surface direction, i.e., the X-Y direction. A multilayer substrate having superior surface flatness can be accurately obtained as a result.

Preferably, green sheets composed of Al_2O_3 or the like that do not sinter at the sintering temperature of the ceramic composition are provided on the upper and lower surfaces, respectively, of the compact, and the compact is preferably sintered while applying pressure or constraint through these green sheets. Here, it is important that the Al_2O_3 green sheets on the upper and lower surfaces of the compact be easily separable and that the metal wiring after the sintering sufficiently adhere onto the ceramic composition so as to avoid conduction failure. Studies were conducted whether this process can be applied to the ceramic composition. The results confirmed that this process can be applied without any problem.

(EXAMPLES)

The starting material powders of the respective components were adequately weighed to give ceramic compositions having compositions shown in Tables 1 to 5. The starting material powders were all oxides. Deionized water was added to the starting material powders, and the resulting mixture was wet-mixed for 20 hours in a ball mill containing zirconia balls.

The resulting mixture was dried and calcined at 700°C

for 2 hours. The calcined mixture was pulverized to obtain a calcined powder. The calcined powder was combined with 10 mass% of a PVA aqueous solution serving as a binder, and the resulting mixture was kneaded, granulated, and press-formed into a compact having a diameter of 15 mm and a height of 7.5 mm. However, Samples 60, 61, and 62 shown in Table 3 were prepared by melting the materials excluding the filler by heating to 1,300°C, rapidly cooling the resulting materials to form a glass frit, adding a predetermined amount of the filler to the glass frit, adding 10 mass% of a PVA aqueous solution serving as a binder to the resulting mixture, kneading and granulating the resulting mixture, and press-forming the resulting mixture into a compact having a diameter of 15 mm and a height of 7.5 mm.

These press-formed compacts were used as the samples. The temperature at which an experimental sintered compact prepared by sintering in the temperature range of 800°C to 1,250°C is sufficiently dense is selected, and each sample was sintered at the corresponding selected temperature. Sintering of the sample was conducted after the sample was heated in air at 500°C to 600°C to remove the binder. The sintering of the sample was conducted by heating the sample at the above-described selected temperature for 2 hours.

The resulting cylindrical sinters were each polished to prepare a flat and smooth setter surface and then analyzed

by a dielectric resonator method (short-circuited at both ends of a dielectric resonator) to determine the relative dielectric constant εr and the Q value ($Q = 1/\tan\delta$). Since the dielectric loss varies depending on the measurement resonant frequency fo, the dielectric loss was evaluated in terms of the fQ value, which is a product of fo and Q and is a constant value dependent on the material of the sample but independent from the frequency. The temperature characteristic τf of the resonance frequency was determined from the rate of change in resonant frequency with varying temperature with reference to the resonant frequency fo at 25°C. The results of the measurement are shown in Tables 1 to 5.

Table 1

Sample No.	Composition of ceramic composition (molar ratio)						Sintering temperature (°C)	Characteristics of ceramic composition				Remarks
	Ln_2O_3 (Ln: Rare earth element)	B_2O_3	RO (R: Alkaline earth metal element)	WO_3	M_2O (M: Alkali metal element)	Filler (Al_2O_3 or TiO_2)		Relative dielectric constant ε_r	fQ (GHz)	Temperature characteristic τ_f (ppm/°C)	Resonant frequency f_0 (GHz)	
1	La_2O_3:*0.1000	*0.9000	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	800	9.1	7500	-41	13.5	Comparative Example
2	La_2O_3: 0.1500	0.8500	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	825	9.5	16500	-36	13.2	Invention Example
3	La_2O_3: 0.2500	0.7500	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	850	10.1	15600	-35	13.0	Invention Example
4	La_2O_3: 0.3333	0.6667	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	850	10.0	16000	-20	12.0	Invention Example
5	La_2O_3: 0.4000	0.6000	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	900	11.0	17500	-15	12.9	Invention Example
6	La_2O_3: 0.5000	0.5000	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	950	11.5	21000	-17	12.7	Invention Example
7	La_2O_3:*0.6000	*0.4000	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	1200	11.8	10200	-25	12.4	Comparative Example
8	La_2O_3:*0.6667	*0.3333	CaO: 0.0500	0.0100	0	Al_2O_3: 0.2000	1250	10.3	15000	-20	13.5	Comparative Example
9	La_2O_3: 0.2500	0.7500	*0	0.0100	0	Al_2O_3: 0.2000	1150	11.8	17000	-25	12.0	Comparative Example
10	La_2O_3: 0.2500	0.7500	CaO: 0.0100	0.0100	0	Al_2O_3: 0.2000	1000	11.5	17500	-30	11.7	Invention Example
11	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.2000	950	11.7	17200	-37	11.2	Invention Example
12	La_2O_3: 0.2500	0.7500	CaO: 0.2000	0.0100	0	Al_2O_3: 0.2000	900	11.4	16800	-42	11.4	Invention Example
13	La_2O_3: 0.2500	0.7500	CaO:*0.2500	0.0100	0	Al_2O_3: 0.2000	950	10.2	15800	-73	13.1	Comparative Example
14	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.2000	900	11.8	16800	-31	11.4	Invention Example
15	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.2000	900	10.0	17200	-31	12.7	Invention Example
16	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0300	0	Al_2O_3: 0.2000	850	10.2	18500	-35	12.4	Invention Example
17	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0500	0	Al_2O_3: 0.2000	850	10.1	17500	-39	12.8	Invention Example
18	La_2O_3: 0.2500	0.7500	CaO: 0.1000	*0.0700	0	Al_2O_3: 0.2000	850	9.8	7200	-59	13.1	Comparative Example
19	La_2O_3: 0.2500	0.7500	CaO: 0.1000	*0.1000	0	Al_2O_3: 0.2000	850	9.8	4300	-70	13.1	Comparative Example
20	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.1000	850	9.2	17400	-32	12.2	Invention Example
21	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.3000	900	9.1	18000	-37	13.0	Invention Example
22	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.4000	950	8.5	18100	-38	13.9	Invention Example
23	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.5500	1100	7.8	12000	-29	14.0	Comparative Example
24	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.6000	1150	7.1	9500	-13	14.1	Comparative Example
25	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	Al_2O_3: 0.1000	910	10.0	16500	-31	12.1	Invention Example

Asterisks indicate that the marked features are outside the scope of the present invention.

Table 2

Sample No.	Composition of ceramic composition (molar ratio)						Sintering temperature (°C)	Characteristics of ceramic composition				Remarks
	Ln_2O_3 (Ln: Rare earth element)	B_2O_3	RO (R: Alkaline earth metal element)	WO_3	M_2O (M: Alkali metal element)	Filler (Al_2O_3 or TiO_2)		Relative dielectric constant ε_r	fQ (GHz)	Temperature characteristic τ_f (ppm/°C)	Resonant frequency f_0 (GHz)	
26	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	TiO_2: 0.3000	915	12.1	17200	-25	12.4	Invention Example
27	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	TiO_2: 0.4000	950	14.1	15000	-20	11.8	Invention Example
28	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	0	TiO_2:*0.5000	1125	14.3	9300	-25	11.1	Comparative Example
29	Nd_2O_3:*0.1000	*0.9000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	850	9.3	7200	-36	13.8	Comparative Example
30	Nd_2O_3: 0.1500	0.8500	CaO: 0.1000	0	0	Al_2O_3: 0.1500	900	10.2	16800	-39	12.4	Invention Example
31	Nd_2O_3: 0.2500	0.7500	CaO: 0.1000	0	0	Al_2O_3: 0.1500	925	10.8	17500	-30	12.1	Invention Example
32	Nd_2O_3: 0.3300	0.6700	CaO: 0.1000	0	0	Al_2O_3: 0.1500	925	11.0	16000	-25	11.0	Invention Example
33	Nd_2O_3: 0.4000	0.6000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	950	12.0	18000	-20	11.2	Invention Example
34	Nd_2O_3: 0.5000	0.5000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	950	11.8	17500	-15	11.5	Invention Example
35	Nd_2O_3: 0.5500	0.4500	CaO: 0.1000	0	0	Al_2O_3: 0.1500	950	11.5	15200	-14	11.7	Invention Example
36	Nd_2O_3:*0.6000	*0.4000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	1050	10.1	11300	-21	10.9	Comparative Example
37	La_2O_3: 0.1000 Nd_2O_3: 0.1000	0.8000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	900	10.5	17500	-30	12.2	Invention Example
38	La_2O_3: 0.2000 Nd_2O_3: 0.2000	0.6000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	950	11.8	18000	-18	11.9	Invention Example
39	La_2O_3: 0.3000 Nd_2O_3: 0.2000	0.5000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	900	11.7	17000	-14	11.6	Invention Example
40	La_2O_3: 0.3000 Nd_2O_3: 0.2000	0.5000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	900	11.8	18000	-13	11.5	Invention Example
41	La_2O_3:*0.3000 Nd_2O_3:*0.3000	*0.4000	CaO: 0.1000	0	0	Al_2O_3: 0.1500	1025	9.8	6300	-21	14.3	Comparative Example
42	La_2O_3: 0.3333	0.6667	BaO: 0.1000	0	0	Al_2O_3: 0.1500	950	10.6	15600	-35	10.1	Invention Example
43	La_2O_3: 0.3333	0.6667	BaO: 0.1000	0	0	Al_2O_3: 0.1500	1000	11.0	15000	-45	11.0	Invention Example
44	La_2O_3: 0.3333	0.6667	BaO:*0.2500	0	0	Al_2O_3: 0.1500	950	11.5	16200	-71	11.1	Comparative Example
45	La_2O_3: 0.3333	0.6667	SrO: 0.0100	0	0	Al_2O_3: 0.1500	1000	9.9	15000	-38	10.2	Invention Example

Asterisks indicate that the marked features are outside the scope of the present invention.

Table 3

Sample No.	Composition of ceramic composition (molar ratio)						Sintering temperature (°C)	Characteristics of ceramic composition				Remarks
	Ln_2O_3 (Ln: Rare earth element)	B_2O_3	RO (R: Alkaline earth metal element)	WO_3	M_2O (M: Alkali metal element)	Filler (Al_2O_3 or TiO_2)		Relative dielectric constant ε_r	fQ (GHz)	Temperature characteristic τ_f (ppm/°C)	Resonant frequency f_0 (GHz)	
46	La_2O_3: 0.3333	0.6667	SrO: 0.1000	0	0	Al_2O_3: 0.1500	1000	10.2	15000	-35	10.2	Invention Example
47	La_2O_3: 0.3333	0.6667	SrO:*0.2500	0	0	Al_2O_3: 0.1500	950	10.8	12500	-70	10.2	Comparative Example
48	La_2O_3: 0.3333	0.6667	CaO: 0.0500 BaO: 0.0100	0	0	Al_2O_3: 0.1500	980	11.0	15200	-45	10.2	Invention Example
49	La_2O_3: 0.3333	0.6667	CaO: 0.1000 BaO: 0.0500	0	0	Al_2O_3: 0.1500	980	11.5	15000	-38	9.8	Invention Example
50	La_2O_3: 0.3333	0.6667	CaO: 0.1000 SrO: 0.0500	0	0	Al_2O_3: 0.1500	950	10.2	15000	-35	10.0	Invention Example
51	La_2O_3: 0.3333	0.6667	BaO: 0.0100 SrO: 0.0500	0	0	Al_2O_3: 0.1500	980	11.5	15000	-40	10.1	Invention Example
52	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0	Li_2O: 0.0010	Al_2O_3: 0.1500	900	11.7	14500	-38	9.8	Invention Example
53	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0	Li_2O: 0.0020	Al_2O_3: 0.1500	850	9.8	15500	-40	8.0	Invention Example
54	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0	Li_2O:*0.0025	Al_2O_3: 0.1500	800	6.8	<2000	Immeasurable	7.8	Comparative Example
55	La_2O_3: 0.2500	0.7500	BaO: 0.0100	0	Li_2O: 0.0010	Al_2O_3: 0.1500	900	12.0	15100	-35	10.1	Invention Example
56	La_2O_3: 0.3333	0.6667	SrO: 0.1000	0	Li_2O: 0.0010	Al_2O_3: 0.1500	850	11.0	15300	-39	10.5	Invention Example
57	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	Na_2O: 0.0010	Al_2O_3: 0.1500	850	10.2	15000	-35	11.3	Invention Example
58	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	Na_2O: 0.0020	Al_2O_3: 0.1500	800	8.0	15100	-36	12.1	Invention Example
59	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	Na_2O:*0.0025	Al_2O_3: 0.1500	800	5.0	<2000	Immeasurable	15.8	Comparative Example
60	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	Li_2O: 0.0010 Na_2O: 0.0010	Al_2O_3: 0.1500	**800	8.5	16100	-38	11.8	Invention Example
61	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	Li_2O: 0.0010 K_2O: 0.0010	Al_2O_3: 0.1500	**825	8.8	15000	-40	11.6	Invention Example
62	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	K_2O: 0.0010 Na_2O: 0.0010	Al_2O_3: 0.1500	**825	9.0	15500	-38	11.3	Invention Example

Asterisks indicate that the marked features are outside the scope of the present invention.

Double asterisks indicate that the filler was mixed after preparation of the glass frit, and the resulting mixture was then sintered.

Table 4

Sample No.	Composition of ceramic composition (molar ratio)						Sintering temperature (°C)	Characteristics of ceramic composition				Remarks
	Ln_2O_3 (Ln: Rare earth element)	B_2O_3	RO (R: Alkaline earth metal element)	WO_3	M_2O (M: Alkali metal element)	Filler (Al_2O_3 or TiO_2)		Relative dielectric constant ε_r	fQ (GHz)	Temperature characteristic τ_f (ppm/°C)	Resonant frequency f_0 (GHz)	
63	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	Rb_2O: 0.0010	Al_2O_3: 0.1500	850	8.7	15000	-35	12.1	Invention Example
64	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0	Cs_2O: 0.0010	Al_2O_3: 0.1500	850	8.5	15000	-33	13.0	Invention Example
65	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.1500	850	10.2	16000	-40	12.0	Invention Example
66	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0300	Li_2O: 0.0010	Al_2O_3: 0.1500	850	7.8	15500	-45	13.8	Invention Example
67	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0500	Li_2O: 0.0010	Al_2O_3: 0.1500	850	7.0	15000	-49	13.5	Invention Example
68	La_2O_3: 0.3333	0.6667	CaO: 0.1000	*0.0600	Li_2O: 0.0010	Al_2O_3: 0.1500	800	6.8	9500	-65	14.0	Comparative Example
69	Nd_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0300	Li_2O: 0.0010	Al_2O_3: 0.1500	850	7.5	16000	-41	13.8	Invention Example
70	Nd_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0500	Li_2O: 0.0010	Al_2O_3: 0.1500	800	6.8	15000	-48	13.3	Invention Example
71	Nd_2O_3: 0.3333	0.6667	CaO: 0.1000	*0.0600	Li_2O: 0.0010	Al_2O_3: 0.2000	800	6.3	6300	-68	14.3	Comparative Example
72	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.1000 TiO_2: 0.1000	950	11.3	16800	-33	10.8	Invention Example
73	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.2000 TiO_2: 0.1000	1000	13.1	17200	-35	10.2	Invention Example
74	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.2500 TiO_2: 0.2500	1150	13.8	16000	-38	10.0	Comparative Example
75	Nd_2O_3: 0.2500	0.7500	CaO: 0.0500 BaO: 0.0500	0.0100	Li_2O: 0.0010	Al_2O_3: 0.2000	1000	12.1	16000	-30	10.5	Invention Example
76	La_2O_3: 0.2000 Nd_2O_3: 0.2000	0.6000	CaO: 0.1000 BaO: 0.0500	0.0100	Li_2O: 0.0010 Na_2O: 0.0010	Al_2O_3: 0.1000 TiO_2: 0.1000	900	11.8	15800	-25	11.0	Invention Example
77	La_2O_3: 0.1500 Nd_2O_3: 0.1500	0.7000	CaO: 0.1000 BaO: 0.0500	0.0100	Li_2O: 0.0010	Al_2O_3: 0.3000	950	9.5	15000	-30	12.1	Invention Example
78	La_2O_3: 0.2000 Nd_2O_3: 0.1333	0.6667	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.1000	900	10.0	15500	-35	10.8	Invention Example
79	La_2O_3: 0.2333 Nd_2O_3: 0.1000	0.6667	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.1000	900	10.5	15000	-40	11.5	Invention Example

Asterisks indicate that the marked features are outside the scope of the present invention.

Table 5

Sample No.	Composition of ceramic composition (molar ratio)						Sintering temperature (°C)	Characteristics of ceramic composition				Remarks
	Ln_2O_3 (Ln: Rare earth element)	B_2O_3	RO (R: Alkaline earth metal element)	WO_3	M_2O (M: Alkali metal element)	Filler (Al_2O_3 or TiO_2)		Relative dielectric constant ε_r	fQ (GHz)	Temperature characteristic τ_f (ppm/°C)	Resonant frequency f_0 (GHz)	
80	La_2O_3: 0.3333	0.6667	CaO: 0.0500 BaO: 0.0500	0.0100	Li_2O: 0.0010 Na_2O: 0.0010	Al_2O_3: 0.1000	850	8.5	17500	-38	14.0	Invention Example
81	La_2O_3: 0.2500	0.7500	CaO: 0.1000 SrO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.1000	850	10.3	16500	-35	12.5	Invention Example
82	La_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	Li_2O: 0.0020	Al_2O_3: 0.1000	850	10.2	16500	-36	12.5	Invention Example
83	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.2000 TiO_2: 0.2000	1000	11.5	17000	-30	10.5	Invention Example
84	La_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3:*0.3000 TiO_2:*0.3000	1150	10.8	7400	-35	12.2	Comparative Example
85	Nd_2O_3: 0.2500	0.7500	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.3000	1000	11.0	15000	-33	11.8	Invention Example
86	Nd_2O_3: 0.3333	0.6667	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.4000	1000	11.2	16000	-38	11.2	Invention Example
87	Nd_2O_3: 0.5000	0.5000	CaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.3000	1000	11.1	15800	-35	11.8	Invention Example
88	Nd_2O_3: 0.5000	0.5000	CaO: 0.1000	0.0100	Li_2O: 0.0010 K_2O: 0.0010	Al_2O_3: 0.3000	980	12.1	15000	-30	9.7	Invention Example
89	Nd_2O_3: 0.5000	0.5000	CaO: 0.1000 BaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.3000	950	11.8	16500	-40	11.5	Invention Example
90	Nd_2O_3: 0.5000	0.5000	CaO: 0.1000 BaO: 0.1000	0.0200	Li_2O: 0.0010	Al_2O_3: 0.3000	950	10.5	15500	-41	12.0	Invention Example
91	La_2O_3: 0.2500 Nd_2O_3: 0.2500	0.5000	CaO: 0.1000 BaO: 0.1000	0.0500	Li_2O: 0.0010	Al_2O_3: 0.3000	900	10.3	15000	-38	11.5	Invention Example
92	La_2O_3: 0.3000 Nd_2O_3: 0.2500	0.4500	CaO: 0.1000 BaO: 0.1000	0.0100	Li_2O: 0.0010	Al_2O_3: 0.3000	1000	10.4	15500	-40	10.3	Invention Example

Asterisks indicate that the marked features are outside the scope of the present invention.

The results shown in Table 1 to 5 show that nearly all of the invention examples exhibited an fQ value of 15,000 GHz or more, a low dielectric loss in the high-frequency band, and a resonant frequency temperature coefficient τ_f of within ±50 °C/ppm. This is presumably due to the effect of incorporating Ln_2O_3 into the glass composition together with the filler. At a small Ln_2O_3 content, the fQ value is low, as shown by Samples 1 in Table 1 and Sample 29 in Table 2.

The invention examples produced sufficiently dense sinters having high fQ values even at a sintering temperature of 1,000°C or less. This is because the contents of the Ln_2O_3, RO, Al_2O_3, and TiO_2 are limited within particular ranges. This fact is clearly supported by the results of Samples 7, 8, 9, 23, 24, 28, 36, 41, 47, 74, and 84 compositions which were outside the ranges of the invention, since they did not achieve the target fQ value or they required high sintering temperatures.

RO has an effect of decreasing the sintering temperature. However, at an excessively large RO content, the temperature coefficient τ_f of the resonant frequency tends to be excessively shifted toward the negative side, as shown by Samples 13, 44, and 47.

Incorporation of WO_3 or M_2O decreases the sintering temperature, and WO_3 or M_2O can be effectively used by controlling its content. At an excessively large content,

however, a significant decrease in fQ value or degradation of temperature coefficient τ_f may result, as shown by Samples 18, 19, 54, 59, 68, and 71.

Industrial Applicability

A ceramic composition of the present invention has a low dielectric loss in the high-frequency band and low temperature dependence of the resonant frequency. Moreover, since its characteristics can be exhibited at a low sintering temperature, a metal, such as Ag or Cu, having a low specific resistance can be used as the material for the metal wiring or electrode, and the conductor loss can thus be decreased. The ceramic composition of the present invention is thus suitable for the substrate materials for high-frequency band multilayer substrates and the materials for electronic components.